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(54) Title: PREPARATION OF CELLULOSE AND FERMENTATION OR NUTRIENT PRODUCTS FROM THE BIO-MASS OF WHOLE ANNUAL PLANTS, PREFERABLY CEREALS

#### (57) Abstract

The present invention relates to a process for the manufacture of a cellulose-containing product, whereby the whole biomass from annual cellulose-producing plants, particularly cereals, is treated with alkali.

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# PREPARATION OF CELLULOSE AND FERMENTATION OR NUTRIENT PRODUCTS FROM THE BIOMASS OF WHOLE ANNUAL PLANTS, PREFERABLY CEREALS. DESCRIPTION

#### Technical filed

5 The raw material of today for the preparation of cellulose for paper production is primarily wood pulp. A number of processes are used. They are characterized most of all of high investment costs and a high energy consumption due to high process temperatures with a high working pressure, which results in troublesome discharges to air, land and water recipients.

As a complement to the more and more decreasing supply of wood raw material other cellulose sources, such as energy forests, grass, straw, leguminous plants etc. been tested. In general one has then used the same production technique as used for wood pulp and thereby obtained the same end results upon the environment.

The present invention relates to a reduction of the environmental problems described as well as energy costs by working with another raw material, running the process at a low temperature, a low pressure and a small consumption of chemicals.

As cellulose raw materials annual cereals are primarily used, such as wheat, rye, barley, etc. but also rice, corn, reed, grass and leguminous plants.

In the process the whole biomass is used. The whole biomass of for example wheat, rye, barley can be divided into a straw part (the straw with its stem, leaves and husks) and a grain part (the grain with the core). The straw part is then present as main raw material for the cellulose recovery. The grain part as a main component for the recovery of a nutrient solution, alternatively for the fermentation of alcohols. The embodiment of the invention is described in the flow diagram of appendix 1 and 2.

In the description below the nomenclature "cellulose" is used as a collective name for a number of components of the composition of the biomass. At the combination of straw and grain for the recovery of cellulose as well as a nutrient solution, and alcohol, alternatively, thus the husk fraction is part of this name. The composition of the raw materials is evident from the appendix 3.

The process is controlled by addition of alkali, temperature, and reaction time. As alkali known hydroxides of primarily Na and Ca are used, alone or in combination. In particular Ca(OH)<sub>2</sub> has turned out to be favourable at the returning to the farming land. Purification and recovery of Na, respectively can be made in any method known from the cellulose technique. The temperature can be varied within wide limits from 20°C to close to the boiling point, 95°C. The reaction time is dependent on the addition of alkali and temperature. The process is controlled and run using known technique from the cellulose industry.

The following notifications are used in the examples given below:

pH is determined electrometrically direct in a test sample of the slurry at 20°C, Ac is determined as used, and added alkali, respectively. 10 g of filtrated slurry is diluted to about 100 ml and is titrated using 1/10 N HCl to pH 8.5 (phenolphtale-ine). The amount of 1/10N HCl used is = acidity. rTS is determined refractometrically using a ABBE refractrometer for the sugar industry., OBrix is connected to refraction index and gives directly %TS (dry matter contents) in a sugar solution.

The raw material consists of field harvested crop whole biomass of wheat consisting of 50 % by weight of straw mass and 50 % by weight of grain mass. The variation is normally +10%. In order to obtain internally reproducible laboratory samples field harvested biomass has been threshed and fractionated in a pure straw part and a pure grain part. The fractions are then used together in the weight relationship 50:50. Grinding of the

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fractions has been made on a hammer mill using 2 mm sieve openings.

Embodiment examples.

#### 5 Example 1.

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Relates to the processing of the whole biomass to cellulose part (solid part), and nutrient solution (liquid part) comprising the straw as well as the insoluble nutrients of the grain part which have been converted enzymatically to soluble com-10 pounds such as glucose, proteins and salts. Flow diagram in appendixes 1 and 2. Process: 300 g of biomass (150 g of straw and 150 g of grain part) are ground into 3000 g of water. The pH of the slurry is adjusted to pH about 7 using calcium hydroxide solution. Then 0.25 g of alfa-amylase, Termamyl<sup>R</sup>, 0.25 g of a protease, Neutrase<sup>R</sup>, and 0.5 g of a combination enzyme SP 342 comprising cellulase, gluconase, hemicellulae and protease are added. All the enzymes are manufactured by NOVO, Copenhagen, DK. The slurry is heated to 50 C for 2 hrs. The temperature is raised to  $95\,^{\rm O}$ C for 1 hr and is then cooled to 65°C. pH is adjusted to about 4.5 using 4 g of phosphoric acid. Then 0.4 g of amyloglucosidase (NOVO) are added. The solution is being completely saccharified for 16 hrs, whereupon the enzymes present are inactivated by raising the temperature to 95°C. The slurry is cooled and is separated into one solid and one liquid phase in a screen centrifuge. The solid phase, the fibres, are washed with water. Yield 2,200 g of liquid phase having a 5% DS and 2,200 g of washing solution having a 0.3% DS (return solution for the next production cycle). Yield of syrup: 2,200 g x 5,3 DS. Yield of fibres: 580 g of moist material from the straw and grain parts, which is fed to the cellulose/paperproduction. The amount of fibre obtained, 580 g, is fed into 2,200 g of water and 40 g of Ca(OH)<sub>2</sub>. Analysis of the process liquid: rTS = 1,0, pH = 12.1, Ac = 24. The slurry is kept at  $90-95^{\circ}$ C for about 6 hrs, the a stabilization of the pH and Ac have been obtained. The sturry is adjusted to the original 3,170 g. Analysis: rTS = 1.6, pH =

11.7, Ac = 9.5. Solid and liquid phases are separated in a

screen centrifuge. The fibres are washed using water, and the wash water is returned to a new cycle together with the process liquid having been separated off. The alkali-fibres having been washed are ground using 2 l of water, are neutralized to pH 6.5 using phosphoric acid. The slurry is diluted to 5 l. The pulp is drawn off on a wire cloth and is washed. The cake is dried for 12 hrs at 75°C. Yield: 126 g DS paper pulp. To obtain a higher end concentration of the nutrient solution (5.0% DS) the amount of biomass 300 g can be complemented with a further 150 g of wheat grain only. Hereby an increase of of about 10% nutrient solution is obtained. To another 150 g of wheat grains, i.e. to a total of 450 g of wheat grains, an about 15% nutrient solution is obtained simultaneously as the yield of cellulose increases due to the husk fraction of the wheat grains.

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#### Example 2.

Relates to processing of the whole biomass to paper and alcohol.

Flow diagram appendixes 1 and 2.

20 Process: 300 g of biomass (150 g of straw part, and 150 g of grain part) are fed into 3000 g of water, pH is adjusted to about 7 using some calcium hydroxide solution. Subsequently 0.25 g of alfa-amylase, Termamyl<sup>R</sup>, and 0.25 g of protease, Neutrase<sup>R</sup>, were added. The slurry was heated to 50°C for 0.5 25 hrs. Then the temperature was raised to 95°C for 1 hr. The slurry was then cooled to 65°C and the slurry was adjusted to 3.300 g, and pH was lowered to 4.5 using 4 g of phosphoric acid, whereupon 0.5 g of amyloglucosidase, NOVO, were added. Complete saccharification of the sugar part for 16 hrs, where-30 upon the enzymes were deactivated at 95°C for 0.5 hrs. The slurry was cooled to 35°C and fermented at 35°C for 18 hrs when the release of  ${\tt CO}_{\tt p}$  ceased. From the mash thus obtained 500 g of a distillate containing 10.3% ethanol was distilled off, which gives 51.5 g of 100 % ethanol. The slurry remaining in the fer-35 mentation and distillation column was diluted to 3.300 g. Solid and liquid phases were separated using a screen centrifuge. The fibres were washed using 300 g of water. Yield: 602 g of moist

fibres. These fibres were fed down into 2000 g of water + 15 g of NaOH. The analysis of the process liquid: rTS = 1.4, pH = 11.9; Ac = 21. The slurry was kept at 20 to 22°C for 12 hrs when a stabilization had been obtained. Analysis of the slurry: rTS = 2.5; pH = 11.4; Ac = 6.6. Solid and liquid phases were separated in a screen centrifuge. The fibres were washed using 300 g of water. Yield: Wet fibres 600 g = 128 g DS in the form of paper pulp, which consists of two cellulose components, the composition of which is evident from appendix 3, Raw materials. The process liquid and the wash water are returned to a new cycle.

In order to determine the contribution of the single components in the yield of alcohol, and cellulose-paper, respectively, of the end product a separate processing of wheat grains only, and straw only, respectively been made according to the following-Example A

150 g of wheat grains only were processed in accordance with Example 2 above and were fermented whereby 43.9 g of 100 % eth-20 anol were obtained. The remaining slurry was screened and the husk fraction was washed, dried for 12 hrs at 75°C, which gave 14 g DS. The dried husks were soaked into 200 g of water and were processed to paper in accordance with Example 2. Yield: 10 g of cellulose.

Example B

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150 g of straw only, were processed in accordance with Example 2 above, whereby 7.4 g of 100 % ethanol were obtained. The remaining slurry of straw was separated off, washed, and subsequently processed to paper, whereby 116 g of cellulose were obtained.

In total: Alcohol: 43.9 + 7.4 = 51.3 g Cellulose: 10 + 116 = 126 g

Example 3.

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Relates to comparative processing of whole biomass to paper and alcohol, where the combination enzyme SP 342 is present. 300 q of biomass are fed into 3000 g of water, pH is adjusted to about 7 using some calcium hydroxide solution. Then 0.25 g of alfa-amylase, Termamyl $^{R}$ , 0.25 g of a protease, Neutrase $^{R}$ , and 0.5 g of SP 342 comprising cellulase, hemicellulase, gluconase, and protease are added. The slurry is heated to 50°C for 2 hrs, whereupon the temperature is raised to 95°C for 1 hr and is then cooled to 65°C. The weight is adjusted to 3,300 g and pH is adjusted to 4.5 using 4 g of phosphoric acid. Then 0.4 g of amyloglucosidase are added and complete saccharification took place for 16 hrs. The slurry contained 3,177 g having a rTS = 5.2. The slurry was cooled to  $35^{\circ}$ C, bakery yeast was added and fermentation took place for 18 hrs when the release of  ${\tt CO}_2$ ceased. From the mash 500 g of an alcoholic solution containing 11.22% by weight of ethanol = 56 g of 100 % ethanol was distilled off. The slurry remaining in the vessel was diluted to 3.000 g and was separated in a screen centrifuge. The fibres were washed, whereby 2500 g of a return solution were obtained for a new cycle, and 574 g of moist fibres. These fibres were fed down into 2000 g of water + 15 g of NaOH. The analysis of the process liquid: rTS = 1.3, pH = 11.8; Ac = 20. The slurry was kept at 20 to 22°C for 12 hrs when a stabilization had been obtained. Analysis of the slurry: rTS = 2.4; pH = 11.4; Ac = 25 6.5. Solid and liquid phases were separated. The fibres were washed, whereby 565 g of moist fibres and 2300 g of return liquid were obtained having a rTS = 2.1 for a new cycle. The fibres were ground with 2000 g of water and were neutralized using 5 g of phosphoric acid to pH.6.5. The slurry was diluted to 30 5 L and was drained on a wire screen. The cake was washed. The sheet was dried for 12 hrs at 75°C. Yield: 117 g of cel-lulosepaper pulp DS.

Storage test with preserved biomass using Ca(OH)2
Test material: Totally harvested cut biomass of wheat (harvested during mild rain). The amount of calcium oxide powder

was calculated on the DS of the biomass.

Test:

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The whole biomass consisted of 50% by weight of straw, and 50% by weight of grain. Water content 31%. 100 g of biomass were placed in tight plastic bags and calcium oxide powder was added and mixed into it as a pulverulent skin. The bags were flattened and well closed. 3 samples of each mixture were stored in a dark heating cabinet at the temperatures given.

15	Sample	Tonnocotus	Mildew af	ter	
	% Ca0	Temperature <sup>O</sup> C	1 months	6 months	12 months
	0	20	weak	strong	very strong
	1		none	none	weak
20	2		none	none	none
	5		none	none	none
	0	37	weak	strong	very strong
	1		weak	strong	very strong
25	2		none	none	none
	5		none	none	none

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Paper sheets produced from pulp according to the Examples above were tested.

Preparation: The fibre pulp was diluted to about 1.75 g pulp DS/litre of water. So much slurry was used that the final sheet weighed (surface weight)  $100 \cdot \text{g/m}^2$ . Draining on the wire screen in a sheet former, pressing, drying and conditioning.

The results of the test are evident from the table below:

#### 10 Table

	Test				
Parameters	1	2	3	4	5
Surface weight g/m <sup>2</sup>	100	99	99	98	103
Tensile index Nm/g	40	39	41	40	41
5 Ductile yield %	1.7	1.8	1.2	1.8	2.0
Burst index Pam²/g	2.1	2.0	2.2	2.1	2.3
Opacity (60 g/m <sup>2</sup> )	99.4	99.2	99.1	99.3	98.3
% Na	<0.1	0.60	0.55	1.0	<0.1
% Ca	3.03	0.13	0.15	0.20	<0.1
					-

Test 1: Nutrient solution + paper with Ca(OH)<sub>2</sub>

Test 2: Alcohol + paper with NaOH

Test 3: Alcohol with SP 342 + paper with NaOH

25 Test 4: Straw only + paper with NaOH

Test 5: Preparation of return paper fibres from wood cellulose from paper mill

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CLAIMS

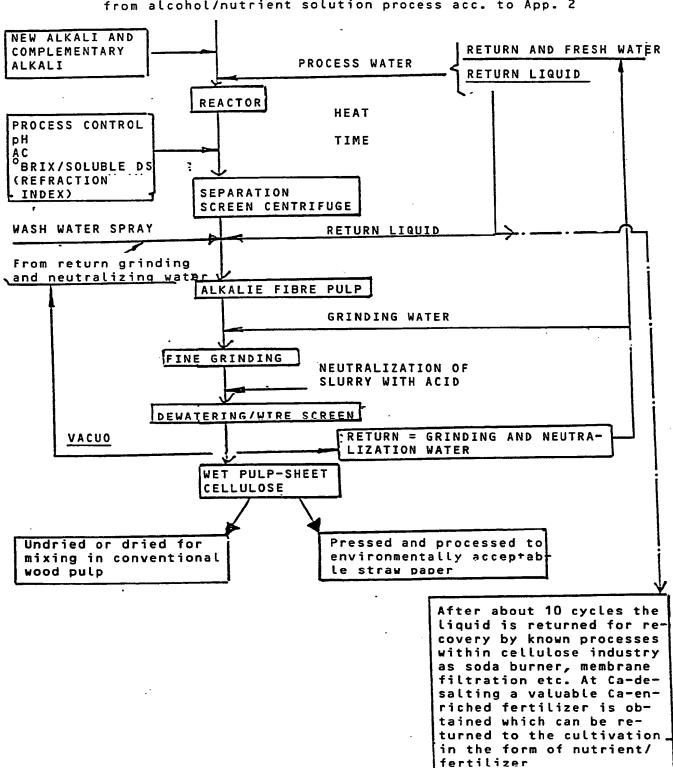
1. Process for the preparation of cellulose containing product, characterized by an alkaline treatment of whole biomass from annual cellulose producing plants, preferably cereals.

- 2. Process according to claim 1, characterized in that the alkaline treatment takes place at a low alkalinity, pH 11.5-13.5 and at a temperature of 20 to  $95^{\circ}$ C.
- 10 3. Process according to claims 1-2, characterized in that one or more of NaOH, Ca(OH)<sub>2</sub>, KOH and NH<sub>3</sub> are used as an alkaline source.
- 4. Process according to claims 1-3, characterized in that an 15 enzymatical treatment takes place prior to a subsequent fermentation to alcohol or isolation of a nutrient solution at the processing of whole biomass.
- 5. Process according to claim 4, characterized in that the bio-20 mass is enzymatically treated with alfa-amylase, amyloglucosidase, protease, and optionally a combined enzyme comprising cellulase, hemicellulase, gluconase and protease.
- 6. Process according to claims 1-3, characterized in that the 25 alkaline treatment of the cellulose content takes place subsequent to the distillation of fermented alcohol, or recovery of nutrient solution, respectively.
- 7. process for the preservation and moist storage of whole bio-30 mass, characterized in that calcium oxide powder is used in an amount of 2 to 5 % calculated on the whole biomass having a water content of 30 %.

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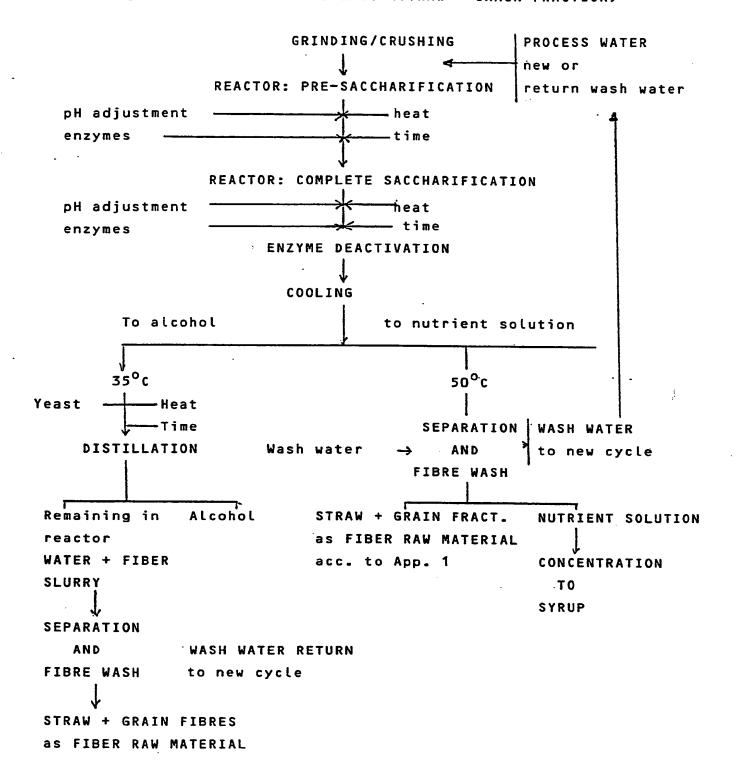
#### FLOW DIAGRAM PULP SHEET

FIBER RAW MATERIAL from alcohol/nutrient solution process acc. to App. 2



Appendix 2.

#### BIOMASS FROM WHOLE CEREALS (STRAW + GRAIN FRACTION)



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Appendix 3.

# RAW MATERIALS Composition in % of DS

Wheat Straw					
Pure cellulose	32	% 27	to	37	
Hemi cellulose	27	23	to	30	
Lignine	21	19	to	24	
Protein	3	2	to	4	
Extractable compounds	10	7	to	12	
Ashes	7	6	to	8	
Total	100				
Husk of the wheat grain					
Pure cellulose	14	%			
Hemi cellulose	44				
Lignine	11				
Protein	15				
Extractable compounds	10				
Ashes	6				
Total	100				
The whole wheat grain					
Starch + sugar compounds	67				
Protein Nx6.25	15				
Husks	13				
Germs + fat	2				
Ashes	4				
Total	100	acc. Ap	pen	dix	1
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### INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 90/00169

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>6</sup>									
According to International Patent Classification (IPC) or to both National Classification and IPC									
IPC5: D 21 C 3/02, C 12 P 7/10, C 12 S 3/02									
II. FIELDS SEARCHED									
	Minimum Documentation Searched <sup>7</sup>								
Classifica	Classification System Classification Symbols								
IPC5	D 21 C; C 12 P								
	Documentation Searched other than Minimum Docuto the Extent that such Documents are included in Field	mentation							
	to the Extent that Such Documents are included in Field	s Searched*							
SE,DK,	FI,NO classes as above	•							
III. DOCL	JMENTS CONSIDERED TO BE RELEVANTS								
Category •	Citation of Document,11 with indication, where appropriate, of the releva	ent passages 12 Relevant to Claim No.13							
Х	SE, C, 137176 (E. ÖMAN) 2 September 1952,								
	see page 1, column 1, line 32 - column 2, line 78	1,2,3							
Y	_,	4,5,6							
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	4 May 1960, see page 1, column 1, line 10 - line 16; page 1, column 1, line 80 - column 2, line 62; page 2,								
v	column 2, line 80 - line 110								
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"A" doc	al categories of cited documents: 10  ument defining the general state of the art which is not sidered to be of particular relevance  "T" later documen or priority date of the art which is not cited to under cited to under	t published after the international filing date a and not in conflict with the application but stand the principle or theory underlying the							
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International Application No. PCT/SE 90/00169

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
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International Application No. PCT/SE 90/00169

FURTHER	INFORMATION CONTINUED FROM THE SECOND SHEET	
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V. X OBSI	ERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE	
	onal search report has not been established in respect of certain claims under Article 17(2) (a)	<del></del>
1. Claim	numbers because they relate to subject matter not required to be searched by this Auth	or the following reasons:
	this Auth	ority, namely:
2. X Claim	numbers because they relate to parts of the instance.	
4. LAJ require	numbers because they relate to parts of the international application that do not comply ments to such an extent that no meaningful international search can be carried out, specifically	with the prescribed
The	invention according to claim 7 is not described to the	
ın s	such a way that a meaningful search can be carried out	•
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10.1000	orro. Rule 6.4(a).	second and third sen-
VI. X OBSE		
	RVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>2</sup>	
This Interna	tional Searching Authority found multiple inventions in this international application as follows:	
i) tiai	m I relates to a process for the manufacture of a cell	ulose-con-
tain	ing product.	
2) Clai	m 7 relates to the preservation and storing of biomass	
	equired additional search fees were timely paid by the applicant, this international search report of the international application.	
2. As only the	some of the required additional search fees were timely paid by the applicant, this international se claims of the international application for which fees were paid, specifically claims:	search report covers
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☐ No prote	st accompanied the payment of additional seach fees.	
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 90/00169

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP fite on 90-05-07 The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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